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(71) Applicant (for all designated States except US): **SAES GETTERS S.P.A. [IT/IT]**; Viale Italia, 77, I-20020 Lianate (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **PUSTERLA, Luca** [IT/IT]; Via Archimede, 42, I-20129 Milano (IT). **SUCCI, Marco** [—/—]; Via Lo Monaco, 9, I-20131 Milano (IT).

(74) Agents: **ADORNO, Silvano**; Società Italiana Brevetti S.p.A., Via Carducci, 8, I-20123 Milano et al. (IT).

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(54) Title: A METHOD FOR MEASURING THE TOTAL CONCENTRATION OF CARBON MONOXIDE AND HYDROCARBONS IN OXYGEN BY MEANS OF ION MOBILITY SPECTROMETRY

(57) Abstract: A method is disclosed for the quantitative analysis of the contents, in oxygen, of carbon monoxide, methane and higher hydrocarbons, by means of ion mobility spectrometry, consisting in converting these species, present in the oxygen flow, into carbon dioxide, measuring the concentration of this latter gas and deducing from this measurement the initial concentration of the oxidizable species.

"A METHOD FOR MEASURING THE TOTAL CONCENTRATION OF CARBON MONOXIDE AND HYDROCARBONS IN OXYGEN BY MEANS OF ION MOBILITY SPECTROMETRY"

5 The present invention relates to a method for measuring the total concentration of carbon monoxide and hydrocarbons in oxygen by means of ion mobility spectrometry.

Oxygen is widely employed as a reacting gas in the integrated circuits industry, in order to build up oxide layers generally acting as an electric insulation between 10 different active portions of a circuit. As is known, in the manufacture of these devices, the purity of all the used materials has a basic importance; as a matter of fact, contaminants possibly present in the reactants or in the reaction environment may be incorporated into the solid state devices, thus altering their electrical features and giving rise to a production wastes. The purity specification of the gases employed in 15 the manufacturing process may change among different manufacturers and depending on the specific process the gas is employed in. Generally, a gas is considered to be acceptable for manufacturing purposes when its impurities content does not exceed 10 ppb (parts per billion, namely an impurity molecule per 10^9 total gas molecules); preferably, the impurities content is lower than 1 ppb. It becomes thus important the 20 possibility to measure extremely low concentrations of impurities in the gases in an accurate and reproducible way.

A technique that can be exploited for such purpose is ion mobility spectrometry, known in the art under the abbreviation IMS; the same abbreviation is also used for the instrument the technique is performed with, while indicating, in this case, "Ion Mobility Spectrometer". The interest in such a technique comes from its extremely 25 high sensitivity, associated with limited size and cost of the instrument; by operating in suitable conditions, it is possible to detect species, in the gas or vapor phase, in a gas medium, in amounts of the picogram order (pg, namely 10^{-12} g) or in concentrations of the order of parts per trillion (ppt, equivalent to one molecule of 30 analyzed substance per 10^{12} molecules of sample gas). IMS instruments and analytical methods in which they are employed, are disclosed, for instance, in US patents 5,457,316 and 5,955,886, assigned to the US firm PCP Inc.

The physicochemical grounds of the technique are very complicated, just as the interpretation of the IMS analytical results. For an explanation of these grounds and results, reference can be made to the book "Ion Mobility Spectrometry" by G.A. Eiceman and Z. Karpas, published in 1994 by CRC Press.

5 Briefly, an IMS instrument essentially consists of a reaction zone, a separation zone and a charged particles collector.

10 Within the reaction zone, there occurs the ionization of the sample, comprising gases or vapors to be analyzed in a carrier gas, usually by means of β -radiations emitted by ^{63}Ni . The ionization mainly occurs on the carrier gas, with the formation of 10 the so-called "reactant ions", whose charge is then distributed to the present species depending on their electron or proton affinities or on their ionization potentials.

15 The reaction zone is divided from the separation one by means of a grid which prevents, when maintained at a suitable potential, the ions produced in the reaction zone from entering into the separation zone. The analysis "time zero" is established by the moment when the grid potential is annulled, thus allowing the ions admission into the separation zone.

20 The separation zone comprises a series of electrodes which create such an electric field that the ions are carried from the grid towards the collector. In this zone, maintained at atmospheric pressure, a gas flow is present having opposite direction 20 with respect to the one of the ion movement. The counterflow gas (defined in the field as "drift gas") is an extremely pure gas, that may either correspond to the gas the impurities content of which has to be determined, or be a different gas. The motion velocity of the ions depends on the electric field and on the cross-section of the same ions in the gaseous medium, so that different ions take different times for crossing the 25 separation zone and reaching the particles collector. The time elapsed from "time zero" to the time of arrival on the particles collector is called "time of flight". The collector is connected to the signal processing system, which transforms the current values sensed as a function of time into the final graph, where peaks corresponding to the different ions are shown as a function of the "time of flight"; from the 30 determination of this time and the knowledge of the test conditions, it is possible to trace the presence of the substances which are object of the analysis, whereas from the peak areas it is possible to calculate, through suitable computation algorithms, the

concentration of the corresponding species.

In the most common mode, an IMS analysis is carried out on species having a positive charge. In the case of oxygen, on the contrary, this also forms negative species in the reaction zone. Under such conditions, (negative mode), in the IMS analysis can only be sensed species having electron affinity higher than oxygen and are then able to receive a charge from this gas; this essentially occurs in the case of carbon dioxide, CO₂. The analysis of impurities in oxygen is therefore limited. Among the species the concentration of which in oxygen is interesting to measure, there are for instance carbon monoxide, CO, and hydrocarbons, among which particularly methane, CH₄.

Object of the present invention is to provide a method of measuring the total concentration of CO and hydrocarbons in oxygen by means of ion mobility spectrometry.

According to the present invention, said object is reached through a method comprising the following operations:

a) converting carbon monoxide and hydrocarbons, present in the oxygen flow, into carbon dioxide;

b) measuring the concentration of carbon dioxide in oxygen after the conversion according to point a); and

c) deducing from the measurement of operation b) the total initial concentration of carbon monoxide and hydrocarbons.

According to a second embodiment thereof, the method of the invention is employed in the case of oxygen containing, already initially, carbon dioxide as an impurity (such condition can be ascertained through a preliminary indicative test performed on oxygen without previously submitting the same to the conversion operation of CO and hydrocarbons). In this case, in the IMS analysis, a concentration value will be obtained corresponding to the sum of the originally present CO₂ and that coming from the conversion of CO and hydrocarbons. In this case, a variation of the method of the invention is employed comprising the following operations:

a) converting carbon monoxide and hydrocarbons, present in the oxygen flow, into carbon dioxide;

b) measuring the concentration of carbon dioxide in the oxygen flow after the

conversion according to point a);

b') performing a further measurement of carbon dioxide concentration in the oxygen flow not submitted to the conversion operation according to point a);

5 c) deducing, from the comparison of the carbon dioxide concentrations measured in operations b) and b'), the initial concentration of carbon monoxide and hydrocarbons.

The invention will be described in the following with reference to the sole figure, schematically showing a system for practically carrying out the method of the invention.

10 According to the method of the invention, CO and hydrocarbons, which are species not detectable in oxygen by a standard IMS analysis, are quantitatively transformed into carbon dioxide, CO₂, which on the contrary is the measurable species in this analysis.

15 The method of the invention may be put into practice by using the gas treatment system schematized in Fig. 1. System 10 is consisting of an inlet line 11 for the gas under examination; along line 11 a system 12 is arranged for converting CO and hydrocarbons into CO₂; system 10 further comprises, upstream and downstream system 12, two three-way valves, V₁ and V₂, that allow the insulation of system 12 from the gas flow, deviating the latter along secondary line 11'. Downstream system 20 12 or line 11' the IMS analyzer 13 is present; this is consisting of the reaction zone 14, divided from the separation zone 15 through grid 16; at the end of zone 15 opposite to zone 14, a particle collector 17 is arranged (no further details, like inlet and outlet openings for the "drift gas", are shown); the collector is electrically connected to unit 18, comprising an electronic section, for the transformation of 25 electrical pulses from collector 17 into numerical data, and a computation section (for example a microprocessor) for processing these data; unit 18 may be physically integrated into a single body with the IMS instrument; finally, unit 18 produces, as an analysis result, spectrum 19, where peaks are recorded corresponding to the different chemical species sensed as a function of their time of flight in instrument 13.

30 In the first embodiment of the method according to the invention, the whole oxygen flow entering system 10 is sent to conversion system 12 by suitably operating valves V₁ and V₂, the conversion of CO and hydrocarbons is carried out, and the so

treated gas is sent to IMS analyzer 13 in order to carry out the analysis.

In the second embodiment of the method according to the invention, operation b) is carried out as in the case of the first embodiment, while operation b') is carried out sending the whole oxygen flow entering system 10 to the analyzer 13 through line 5 11', insulating system 12 by suitably operating valves V₁ and V₂ in this case too.

System 12 for the conversion of CO and hydrocarbons to CO₂ comprises at least one oxidation catalyst compound; continuous regeneration of such a compound is favoured in that CO and hydrocarbons are present as traces in an atmosphere nearly completely consisting of oxygen. Catalyst compounds useful for this conversion are 10 for instance the oxides of some noble metals, like ruthenium, rhodium, palladium and platinum; among these, palladium oxide, PdO, is preferred. The optimal working temperature of PdO is between about 200 and about 350 °C. Palladium oxide or even complete systems for the conversion of CO and hydrocarbons containing this compound, are commercially available and sold for instance by the Applicant, by the 15 German firm Degussa-Hüls AG and by the US firm Engelhard Co.

CLAIMS

1. A method for measuring the concentration of carbon monoxide and hydrocarbons in oxygen by means of ion mobility spectrometry, comprising the following operations:
 - 5 a) converting carbon monoxide and hydrocarbons, present in the oxygen flow, to carbon dioxide;
 - b) measuring the concentration of carbon dioxide in oxygen after the conversion of point a); and
 - c) deducing from the measurement of operation b) the total initial concentration 10 of carbon monoxide and hydrocarbons.
2. A method according to claim 1, further comprising an operation b'), consisting in carrying out a further measurement of carbon dioxide concentration in the oxygen flow not submitted to the conversion operation a); and wherein operation c) is performed by comparing the carbon dioxide concentrations measured in 15 operations b) and b').
3. A method according to claim 1, wherein operation a) is carried out by employing a system (10) for the gas treatment, consisting of an inlet line (11) for the gas under examination, a system (12) for converting carbon monoxide and hydrocarbons, an IMS analyzer (13) and a sensing and data processing unit (18), by sending the whole gaseous flow entering said treatment system to the system for the conversion of carbon monoxide and hydrocarbons by suitably operating two three-way valves (V₁; V₂), arranged upstream and downstream said conversion system. 20
4. A method according to claim 2, wherein operation b') is carried out employing a system (10) for the gas treatment, consisting of an inlet line (11) for the gas under examination, a system (12) for converting carbon monoxide and hydrocarbons, an IMS analyzer (13) and a sensing and data processing unit (18), by sending the whole gaseous flow entering said treatment system to the analyzer through a secondary line (11') and avoiding the passage through said system for converting carbon monoxide and hydrocarbons, by suitably operating two three-way valves (V₁; V₂) arranged upstream and downstream said conversion system. 25
- 30 5. A method according to either of claims 3 and 4, wherein said system for converting carbon monoxide and hydrocarbons comprises at least one catalyst

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compound, active in hydrocarbons oxidation, selected among the noble metal oxides.

6. A method according to claim 5, wherein said compound is palladium oxide.

7. A method according to claim 6, wherein palladium oxide is maintained, during operation b), at a temperature comprised between 200 and 350°C.

